Small scale structured BaTiO₃-based coatings for catalytic applications

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Introduction

Integration of precious metal in perovskite structures (BaTiO₃PM, M = Pd, Rh, etc) results in more ageing resistance and higher N₂-selective catalysts compared to the precious metals supported on single oxides under temperatures exceeding 800°-900°C [1]. Homogeneous dispersed ion metals (i.e. Pt, Pd, Rh) in perovskite structures can result in more active and selective active sites as well. Here a Ba-based perovskite is prepared starting from different synthesis routes and doped with Pd and Rh. The catalytic properties of Rh and Pd-integrated perovskite are studied.

Sol-gel synthesis of Ba-based perovskite

BaTi(1-x)PdO₃ powder, using metallic Ba, Ti-isopropoxide and Pd(NO₃)

- Pd-substituted BaTiO₃-perovskite crystallizes at 500°C
- Traces of BaCO₃ present even after calcination at 900°C

BaTi(1-x)RhO₃ powder, using Ba(NO₃)

- Crystallization of cubic BaTiO₃ at 700°C
- Rhombohedral and hexagonal BaTiO₃ with traces of BaO after 700°C

BaTiO₃ coating on Ti-substrates, using Ba(NO₃) and Ti-isopropoxide

- BaTiO₃ coatings on Ti substrates
- Crystallization of BaTiO₃ at 160°C

TEM and EDX analysis for identification of precious metal

 Visualization difficulty due to none contrast between BaTiO₃ and 7.2 vol. % CO₂
 Effect of catalyst calcination temperature on NO₃ reduction
 Reaction conditions: 720 ppm NO, 1 vol. % H₂, 5 vol. % O₂, 7.2 vol. % H₂O and 7.2 vol. % CO₂, He as balance gas, SV = 55 200 h⁻¹

XPS analysis

1. Strong basicity on barium surface due to carbonates,
2. Ti-enrichment at the surface upon reduction treatment at 200°C,
3. The asymmetric lines for palladium indicate the presence of multiple ionic species, i.e. Pd intra-crystalline, Pd²⁺, Pd⁰,

H₂-Selective Catalytic Reduction of NOx
NOx-conversion and N₂-selectivity

Effect of reaction temperature on NO₃-reduction
Reaction conditions: Lean: 8500 ppm O₂, Stoichiometric: 1.1 % CO, 1000 ppm NO, 9500 ppm O₂, He balance, Rich: 10500 ppm O₂

Conclusions and outlook

- Formation of crystal phase(s) from BaTiO₃ perovskite sols is strongly influenced by the applied synthesis route,
- Hexagonal-shaped BaTiO₃-crystals grow on dip-coating of metallic substrates with modified BaTiO₃-sol at temperatures as low as 160°C,
- Pd or Rh can be integrated into BaTiO₃, perovskite by sol-gel route,
- XPS indicates that Pd-states corresponding to both PdO and Pd intra-crystalline (Pd³⁺) are present in BaTiPdO₃,
- It is a challenging task to identify Pd in BaTiO₃ matrix (due to non-conductivity of the sample, size of the Pd-particles, Pd-ions in the crystal or on the perovskite surface). These problems were overcome by applying the energy filtering TEM working method,
- Pd and Rh integrated BaTiO₃ are promising catalysts for NO₂-reduction under rich and lean conditions; BaTiPdO₃ yields 80 to 90 % of NO₂-reduction and ca. 80 % selectivity to N₂ at 200°C under H₂-SCR conditions, BaTi₁ₓRh₁₋ₓO₃ is very active between 100° and 200°C under rich conditions for NO reduction over CO + NO reaction.